In-situ scattering study of a liquid-liquid phase transition in Fe-B-Nb-Y supercooled liquids and its correlation with glass-forming ability

Jiacheng Ge a, Haiyan He b, Jing Zhou c, Chenyu Lu b, Weixia Dong a, Sinan Liu a, Si Lan c, b, *, Zhenduo Wu b, Anding Wang d, Liang Wang e, Cun Yu f, Baolong Shen c, **, Xun-li Wang b, g, ***

* Corresponding author. Herbert Gleiter Institute of Nanoscience, School of Materials Science and Engineering, Nanjing University of Science and Technology, 200 Xiaolingwei Avenue, Nanjing, China.
** Corresponding author. Department of Physics, City University of Hong Kong, 83 Tat Chee Avenue, Kowloon, Hong Kong, China.
*** Corresponding author. Department of Physics, City University of Hong Kong, 83 Tat Chee Avenue, Kowloon, Hong Kong, China.
E-mail addresses: lansi@njust.edu.cn (S. Lan), blshen@seu.edu.cn (B. Shen), xlwang@cityu.edu.hk (X.-l. Wang).

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ABSTRACT

In-situ synchrotron high-energy X-ray diffraction was used to study the kinetics of structure evolution for two Fe-based bulk metallic glasses with different thermophysical behaviors upon heating and isothermal annealing in the supercooled liquid region. It is found that the structure change of (Fe0.72B0.24Nb0.04)97Y3, an average glass former, follows a continuous disordering process before crystallization, while that of (Fe0.72B0.24Nb0.04)95.5Y4.5, a better glass former with an anomalous exothermic peak below the crystallization temperature, is characterized by a reentrant supercooled liquid behavior. A hidden amorphous phase with a configurationally highly-correlated structure is found at a critical temperature of the anomalous exothermic peak for the (Fe0.72B0.24Nb0.04)95.5Y4.5 supercooled liquid, and then it reenters the disordered phase of lower correlation length at a higher temperature. Synchrotron diffraction and the density measurements together illustrate that the liquid-liquid phase transition accompanies with an unusual density change upon isothermal annealing at the anomalous exothermic peak temperature. Our experimental results suggest that a liquid-liquid phase transition which occurred at the medium-range length scale plays an important role in stabilizing the (Fe0.72B0.24Nb0.04)95.5Y4.5 supercooled liquid. Possible mechanisms for the observed differences and the relationship with the glass-forming ability are discussed based on the results of the pair distribution function analysis.

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1. Introduction

Liquids/glasses, like their crystalline counterparts, can have polymorphs. Liquid-liquid phase transition (LLPT) means that the liquids with the same composition but different locally favored structures (LFSs) can transform to each other upon cooling/heating [1]. LLPT has been found to be a universal phenomenon [2,3]. However, the origin of LLPT remains elusive and even controversial. The cooperative arrangement of bond-orientation orders, that is, LFSs, upon cooling/heating has been proposed to be responsible for the LLPT in molecular liquids such as water [4] and triphenyl phosphite (TPP) [5]. The LLPT in atomic liquids was suggested to occur at high temperature [6] and pressure [7]. Recently, a hidden LLPT was revealed in Pd-Ni-P bulk metallic glasses (BMGs) accompanied by an anomalous exothermic peak (AEP) upon heating [8]. The AEP was identified to be located in the supercooled...
liquid region, which is just above the glass transition temperature \( T_g \) and far below the crystallization temperature \( T_x \).

It has been found that the AEP also exists in a variety of BMGs, including Zr-based \([9–13]\), Fe-based \([14]\), Mg-based \([15]\), and Ni-based alloys \([16]\), etc. The AEP in BMGs attracted much attention because it opens a window to build up a correlation between the hidden phase transitions and glass-forming ability (GFA). For example, Fe-B-Nb-Y BMGs with an AEP has good soft magnetic property (e.g., low coercivity) and excellent GFA \([14]\). Studies have been done, mostly by ex-situ characterizations, to investigate the structure change at short-range order (SRO) \([17]\). However, more and more evidence indicated that the structure change beyond the short-range length scale plays a more critical role in phase transitions, including LLPT \([8,18]\), crystallization \([3,19]\), etc. Therefore it is desirable to in-situ study the hidden LLPT and probe the structural evolution at multiple length scales, from short-range to medium-range and nanoscale, for the Fe-based BMGs in the temperature region of the AEP.

In this paper, the experimental evidence was obtained for the hidden LLPT which occurred in the same temperature region of AEP in the supercooled liquid region of a Fe-B-Nb-Y BM using in-situ synchrotron high-energy X-ray diffraction (HE-XRD), small-angle X-ray scattering (SAXS) as well as differential scanning calorimetry (DSC). For easy presentation, the studied alloys, ((Fe\(_{0.72}\)B\(_{0.24}\)Nb\(_{0.04}\))\(_{97}\)Y\(_{3}\) and (Fe\(_{0.72}\)B\(_{0.24}\)Nb\(_{0.04}\))\(_{95.5}\)Y\(_{4.5}\), were abbreviated as Y3 and Y4.5. The Y4.5 alloy exhibits an AEP while Y3 does not. Chemical phase separation at nanoscale and crystallization were ruled out in the AEP temperature region of Y4.5. It turns out that the supercooled liquid achieves an ordered state first and then reenters into a more disordered state at a higher temperature above the AEP upon heating. The synchrotron diffraction and density measurements demonstrate that the density of Y4.5 alloy decreases after the LLPT when annealing in the AEP temperature region. The atomic scale structure change at medium-range length scale is found to play an important role during LLPT. Furthermore, it is suggested that the stabilization of the supercooled liquid in the AEP alloy, Y4.5, is correlated with the improved GFA.

2. Experimental

2.1. Sample preparation

Fe (99.9%), B (99.5%), and Nb (99.9%) elements were carefully weighed in the right proportion and were melted by induction to obtain the ingots of Fe\(_{72}\)B\(_{24}\)Nb\(_{4}\). Then Y (99.9%) were weighed and were melted by induction to the right proportion and were melted by induction to obtain the ingots of Fe\(_{72}\)B\(_{24}\)Nb\(_{4}\). The heating rate was 20 K min\(^{-1}\). So the time resolution was around 5 s and the temperature resolution was 1–2 K. The static structure factor, \( S(Q) \) with \( Q_{\text{max}} \approx 30 \text{ Å}^{-1} \), was derived from the scattering data after masking bad pixels, integrating images, subtracting the appropriate background and correcting for oblique incidence, absorption, multiple scattering, fluorescence, Compton scattering, and Laue correction using Fit2D and PDFgetX2. The reduced pair transform of \( S(Q) \), \( G(r) = \frac{2}{\pi} \int_0^{Q_{\text{max}}} Q S(Q) - 1 \sin(Qr)dQ \), where \( r \) is the distance in real space and \( Q = 4 \pi \sin(\lambda) / \lambda \). Here 0.1 s is the time of the scattering angle between the incident beam and the scattered beam. \( \lambda \) is the X-ray wavelength.

SAXS measurements were conducted on the SAXSspace line collimation camera. All samples were cut and thinned to be foils with 30–40 \( \mu \)m thickness to ensure the appropriate transmittance. The sample chamber was evacuated to a vacuum of \( 10^{-3} \) torr to reduce the background noise. The scattering patterns were acquired in a transmission geometry using a 2D detector. The 2D images were integrated azimuthally, corrected for background scattering and normalized using SAXSreat and SAXSquant software (Anton Paar). Density measurement was conducted using a METTER TOLEDO Instructions XP Analytical Balance based on the Archimedes’ principle. The N-Hexadecane-D\(_{34}\) solution was employed during the density measurement. The mass density of Y4.5 alloys before and after treatment was measured repeatedly at least 5 times to reduce the measuring error.

3. Results

3.1. Thermo-physical behavior, AEP, and GFA indicators

Fig. 1 shows the DSC measurement results and the HE-XRD diffraction patterns for Y3 and Y4.5 BMGs. Fig. 1(a) is the scanning curves for Y3 (blue) and Y4.5 (red) BMGs. Thermophysical parameters have been summarized in Table 1. In Y4.5, there is an AEP above the \( T_g \). The valley of the AEP, \( T_C \), is ~908 K. The \( T_g \) for Y4.5 is ~22 K wider than that of Y3, indicating more stable supercooled liquid for Y4.5 alloys.

The calculated GFA indicators for Y4.5, including the reduced glass transition temperature \( T_{\text{rg}} \) and Gamma value \( \gamma \), are larger than those of Y3, which is consistent with the critical casting thickness as shown in Table 1. There is no detectable difference between the DSC curve of the rods and that of ribbons of Y4.5 alloys from Fig. 1(b). Furthermore, the AEP for Y4.5 BMGs disappeared after annealed at \( T_C \) with a period of ~300 s. The \( T_C \) for Y4.5 shifts to ~3878 K, which is ~21 K higher than that of the as-cast Y4.5 BMG and ~33 K higher than that of the as-cast Y3 BMG, suggesting that the Y4.5 achieves a much more stable glassy state after annealing.

3.2. In-situ synchrotron X-ray diffraction study of liquid-liquid phase transition

To gain physical insights into the DSC results, as shown in Fig. 1(c) and (d), in-situ synchrotron HE-XRD measurements were carried out for Y4.5 and Y3 upon heating. The diffraction pattern at ~\( T_C \) shows that the sample is still in the amorphous state. The Rietveld refinement results in Fig. 2(a) and (b) illustrate that the crystalline phase for Y4.5 (B\(_6\)Fe\(_{23}\), space group: Fm-3m) is less ordered than those of Y3 (B\(_8\)Fe\(_{23}\), space group: Fm-3m and BFe\(_{23}\), space group: F4/mcm) after heating to ~1003 K. The HE-XRD results thus confirm that the Y4.5 supercooled liquids are more stable to resist crystallization, which is consistent with the better GFA of Y4.5.
Fig. 3(a) and 3(b) show the structure factor, $S(Q)$, of Y4.5 and Y3 BMGs upon heating. Fig. 3(c) and (d) are their corresponding differential $S(Q)$, which was obtained by subtracting the diffraction pattern at a temperature close to the $T_g$. There is an unusual structure change as indicated by the dotted line for the first sharp diffraction peak (FSDP), $Q_1$, of the $S(Q)$ for the Y4.5 BMG. The differential $S(Q)$ at 905 K, $\sim T_C$, shows an inconsistent profile with those patterns at temperatures above and below $T_C$. However, the differential $S(Q)$ evolves consistently for the Y3 BMG.

Fig. 4 shows the SAXS profiles of Y4.5 at the as-cast state and after annealing at a temperature close to $T_C$, with a period of about 300 s. The developing profiles as a function of $Q$ are almost overlapping with each other, confirming that in the Y4.5 alloy after isothermal annealing there is no resolvable phase separation at the nanoscale ($\sim 40$ nm).

Further peak analysis for the FSDP, $Q_1$, has been done to identify the anomalous structure change for Y4.5 AEP alloy. Fig. 5 shows the results of the first moment and the second moment analysis as a function of temperature, corresponding to the peak position and width respectively [18]. The analysis of moments was often used to avoid the subjectivity of assumed functions for the peak shape of the asymmetric FSDP. Peak position and width of the FSDP were suggested to be linked to the density and correlation length for the glasses/liquids [20]. As shown in Fig. 5(b) and (d), the values of the first and second moments develop linearly above and below the glass transition for Y3 BMGs. However, in Fig. 5(a) and (c), the $Q_1$ value shows a slope change at $T_C$ for Y4.5 BMGs. The anomalous structure change for Y4.5 suggesting a hidden LLPT occurred in association with the AEP at $T_C$. More interestingly, the second moment shows a discontinuous change at $T_C$. The Y4.5 supercooled liquid initially becomes more correlated and then goes back to a less correlated state at a high temperature after $T_C$, indicating the reentrant behavior of the supercooled liquid upon heating.

### Table 1
Thermophysical parameters $T_g$, $T_x$, $T_c$, $T_l$, and critical thickness for Fe-B-Nb-Y BMGs.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$T_g$ (K)</th>
<th>$T_x$ (K)</th>
<th>$T_c$ (K)</th>
<th>$T_l$ (K)</th>
<th>$D_c$ (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Fe}<em>{0.72}\text{B}</em>{0.24}\text{Nb}<em>{0.04}\text{Y}</em>{3}$</td>
<td>845</td>
<td>924, 988</td>
<td>--</td>
<td>1430$^a$</td>
<td>0.591</td>
</tr>
<tr>
<td>$\text{Fe}<em>{0.72}\text{B}</em>{0.24}\text{Nb}<em>{0.04}\text{Y}</em>{4.5}$</td>
<td>857</td>
<td>958,988</td>
<td>908</td>
<td>1349$^a$</td>
<td>0.635</td>
</tr>
</tbody>
</table>

$^a$ From Ref. [14].

Fig. 3(a) and 3(b) show the structure factor, $S(Q)$, of Y4.5 and Y3 BMGs upon heating. Fig. 3(c) and (d) are their corresponding differential $S(Q)$, which was obtained by subtracting the diffraction pattern at a temperature close to the $T_g$. There is an unusual structure change as indicated by the dotted line for the first sharp diffraction peak (FSDP), $Q_1$, of the $S(Q)$ for the Y4.5 BMG. The differential $S(Q)$ at 905 K, $\sim T_C$, shows an inconsistent profile with those patterns at temperatures above and below $T_C$. However, the differential $S(Q)$ evolves consistently for the Y3 BMG.
neighbor shell and can be used to identify the structure information of solute-centered SRO. The shoulder of the second peak, \( r_{22} \), indicates the extended-range order beyond the nearest neighbor shell, that is, packing connectivity [21]. Fig. 6(c) shows the integrated intensity for \( r_1 \) and \( r_{22} \) in \( G(r) \) patterns as a function of annealing time. The intensity of \( r_{22} \) rises while the intensity of \( r_1 \) does not change much during annealing. These changes further demonstrate that the cluster connectivity was enhanced after the LLPT. The correlation between the peak position and the mass density in BMGs was revealed before [20,22,23]. Density can be measured using the fluid displacement method based on the Archimedes’ principle [24]. Fig. 8 shows the value change of \( Q_1 \) under isothermal annealing and the measured density change during the LLPT. The value of \( Q_1 \) is in the right proportion to the mass density, following the relationship, \( Q_1 V_0^{33.2=0.007} = 9.3 \pm 0.2 \) [20]. Moreover, the value of \( Q_1 \) decreases after annealing, and it is coincident with the change of the measured mass density.

4. Discussion

4.1. Effect of the change of the driving force on nucleation after LLPT and the correlation with GFA

Our results suggest a correlation between the AEP and GFA for the soft magnetic Fe-B-Nb-Y BMGs. The AEP in the supercooled liquid region has been studied in Fe-based MGs [14,17,25], but few works relate it with the GFA. The hidden LLPT, which could be brought out upon heating/annealing in the supercooled liquid region, connects the AEP and GFA for the Fe-B-Nb-Y supercooled metallic liquids. According to the glass transition theories [26–30], the cooperative rearrangement of LFSs, that is, short-to-medium range orders (SRO and MRO), would play an important role during the liquid-to-glass transition. Upon heating the Y4.5 to a temperature above \( T_g \) but below \( T_c \), the supercooled liquid transforms from a phase of less correlation length to another phase of larger correlation length. Furthermore, when heating the Y4.5 above \( T_c \) but below \( T_s \), the supercooled liquid, driven by entropy, goes back to the disordered phase with less correlation length at a higher temperature. The unusual growth in a correlation length of the LFSs has been revealed by simulations [31] and experiments [18,32–34] for the metallic glass-forming liquids. Presumably, the newly-formed liquid phase with highly-correlated LFSs in the vicinity of glass transition temperature has slower dynamics (that is, smaller diffusion coefficient or larger overall viscosity) [35] and plays a vital role in stabilizing the supercooled liquids.

The Y4.5 alloys quenched from the supercooled liquid after the occurrence of LLPT has more stable glassy and supercooled liquid states than those of Y3 alloys. There is no AEP for the Y4.5 BMG after annealed at \( -T_c \). Furthermore, the annealed Y4.5 MGs show much higher \( T_g (-33 K) \) and broader supercooled liquid region than those of as-cast Y3 MG, which means the new amorphous phase has a lower energy state and might encounter a higher energy barrier during subsequent crystallization in the Y4.5 supercooled liquid after the occurrence of LLPT. The nucleation rate [36] is defined as a function of chemical potentials (\( \Delta g \)) and interfacial energy (\( \sigma \)) between the precipitates and the amorphous/liquid matrix:

\[
\nu = D \cdot \exp(-W^*/k_BT)
\]  

where \( W^* \) is known as the nucleation barrier, which can be expressed as \( W^* = 16 \pi r^3 / 3 \Delta g \), and \( D \) is the diffusion coefficient. \( \Delta g \) is right proportional to the undercooling, \( \Delta T = (T_s - T) \). Y4.5 alloys have a lower \( T_1 \) than that of Y3 (Table 1). So for the same
crystallization temperature, the $\Delta T$ of Y4.5 is smaller than that of Y3. Therefore, the $\Delta g$ of Y4.5 would be smaller than that of Y3. After the occurrence of the LLPT, the newly-formed supercooled liquid has more correlated LFSs, that is, SRO and MRO. The local symmetry of LFSs is usually different from the crystalline order [37–41]. Presumably, the presence of highly-correlated LFSs would raise the interfacial energy $\sigma$ between the new liquid phase and the crystalline solid for Y4.5 supercooled liquid [27,35,42]. So the nucleation barrier for the Y4.5 supercooled liquid after the occurrence of LLPT would be larger than that of the Y3 supercooled liquid, which thus reduces the nucleation rate.

It was reported that the supercooled liquids of excellent GFA also correspond to a slow growth rate of the crystal embryos due to the ‘pinning’ effect [43] of LFSs. The atomic radius for Fe, Nb, B, Y is 0.126 nm, 0.146 nm, 0.086 nm, and 0.174 nm, respectively [14,44]. The Y element has the largest atomic size among all constituent elements and possesses the slowest mobility among all atoms [45–47]. On the other hand, the enthalpy of mixing for Y-B has a much negative value in the Fe-B-Nb-Y alloy systems, $\approx -50$ kJ mol$^{-1}$, which would enable the formation of stable clusters of local ordering to frustrate the growth of crystal embryos [17]. Furthermore, although thermal stability does not necessarily correlate with GFA [48], stable glass-forming liquids with pronounced SRO and MRO, such as Y4.5 alloys, often have an excellent GFA.

### 4.2. The role of cluster connectivity on LLPT

Our experiment rules out the occurrence of crystallization or chemical phase separation at nanoscale when heating the Y4.5 BMG to the AEP temperature region. The HE-XRD can resolve nanocrystalline phases of a $10^{-3}$ vol fraction [18]. According to the in-situ XRD results (Fig. 3), there is no hint for the occurrence of crystallization at $T_C$. Although the heat of mixing between Y and Nb elements is $+30$ kJ mol$^{-1}$, SAXS measurements in Fig. 4 reveal that...
Fig. 5. Profile analysis results of the first sharp diffraction peak of $S(Q)$. The first moment changes as a function of temperature (a) for Y4.5 alloys and (b) for Y3 alloys. The second moment changes as a function of temperature (c) for Y4.5 alloys and (d) for Y3 alloys. The solid lines serve as a guide to the eyes.

Fig. 6. Real-space analysis of the synchrotron diffraction results. The reduced pair distribution function, $G(r)$, at different temperature upon heating (a) for Y4.5 alloys and (b) for Y3 alloys. The intensity change of the first coordination shell, $r_1$, and the shoulder of the second coordination shell, $r_{22}$, as a function of temperature (c) for Y4.5 alloys and (d) for Y3 alloys. The DSC curves have been superimposed for comparison. The solid lines are the results of a smooth spline fitting. The bands are guide to the eyes.
there is no chemical phase separation at the nanoscale. The TEM studies have been done by Lee et al. [14] for Y4.5 alloys, suggesting that the phase separation can be excluded due to the small contents of both Nb (4 at%) and Y (4.5 at%). However, the addition of Y element is just 1.5 at% in Y4.5 alloys more than that of Y3 alloys, which results in much pronounced r22 peak as shown in Figs. 6 and 7. More interestingly, there is a one-to-one correspondence between the intensity change of the shoulder peak r22 and the evolution of the calorimetric anomaly, that is, the AEP, in the supercooled liquid region, further illustrating the role of cluster connectivity on LLPT [9].

4.3. The structure origin of the density change and the nature of a LLPT

The mass density change in a LLPT of MGs is a controversial issue. Some studies showed that the density tends to increase after the LLPT [49]. However, It was argued by the others that density change is not necessary during the LLPT for some cases [50]. Our experimental results show that there is a density change during the LLPT at Tc. The mass density decreases from 7.218 ± 0.007 to 7.201 ± 0.009 g cm⁻³ during isothermal annealing. The unusual density decrease may be due to the following possible reasons. First, the Fe-B-based alloys have unique SRO clusters [51], which easily connect to be more ordered at medium-range length scale [8,38]. Second, the Y atom has the largest atomic radius and can play a glue/joint atom role in the medium-range packing scale as illustrated by the PDF results. Fig. 9 is the schematic diagram for the possible packing scheme of the SRO clusters at the medium-range length scale before and after LLPT. Before the LLPT, the SRO clusters show a random packing scheme at the medium-range length scale. The Y atoms locate at some sites which are not energy favored states. After the LLPT, the SRO clusters tend to be more ordered and more connective. Therefore, Y glue/joint atoms can play a role on enhancing the connectivity of the clusters as illustrated by the increasing intensity of r22 in Y4.5 alloys after the occurrence of LLPT. However, the local atomic volume somehow could expand when the Y atoms move to energy favored places in the system. Therefore, the density after the LLPT finally decreases and the alloy system after the LLPT tends to be more stable as proved by our experimental results including the calorimetric and density measurements as well as the synchrotron diffraction studies. By consideration of the following evidence, including the structure change, latent heat, and density anomaly, the LLPT in Fe-B-Nb-Y alloys might be a ‘first-order’ type [6,13].
5. Conclusions

In summary, we reveal evidence of the formation of a hidden amorphous phase with configurationally highly-correlated structure in the supercooled liquid region of Fe-B-Nb-Y BMGs of an anomalous exothermic peak using in-situ synchrotron X-ray diffraction measurements. The occurrence of LLPT is associated with an unusual density change. In addition, the new amorphous phase reenters the disordered phase of lower correlation length at a higher temperature during heating. It turns out that the new amorphous phase at $T_C$ stabilizes the supercooled liquid, which might be the structural origin of the good GFA of the Y4.5 alloys. The intensity change of the shoulder peak for the second coordination shell of the pre-amorphous structure further indicates the important role of cluster connectivity on the amorphous phase transition. The structure change, density anomaly, and the latent heat during the transformation around $T_C$ suggest a possible ‘first-order’ nature of the LLPT in the Fe-B-Nb-Y supercooled liquids.

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